Received 00th January 20xx,

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Inverse vulcanization below the melting point of sulfur

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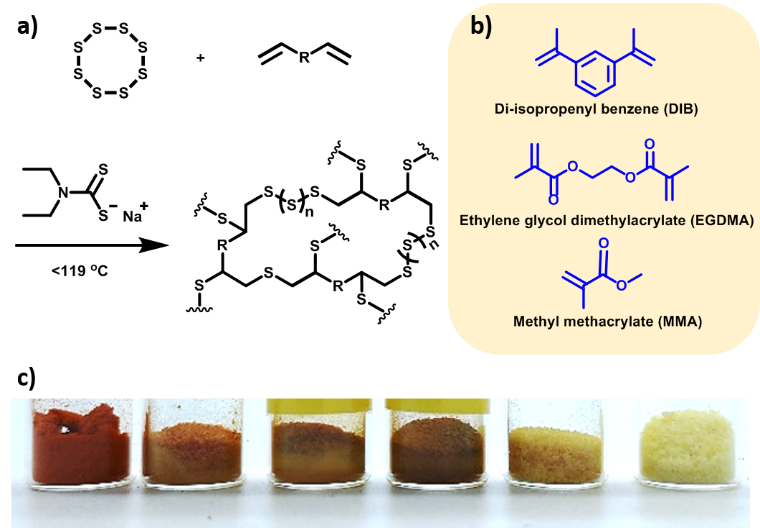


Figure 1. (a) General reaction scheme for the inverse vulcanization below sulfur melting point with catalyst NaDTC. (b) Structure of crosslinkers for inverse vulcanization reported, 1,3-diisopropenylbenzene (DIB), ethylene glycol dimethylacrylate (EGDMA), and methy methacrylate (MMA). (c) Stable solid state products generated from inverse vulcanization below 119 °C. From left to right, ground sulfur polymers of SDIBC0T180, SDIBC1T110, SDIBC5T110, SDIBC10T110, SEGDMAC1T110, and SEGDMAC1T100 (see footnote of table 1 for naming system)

**Elemental sulfur is an abundant by-product of the petrochemicals industry, but polymers formed from pure sulfur cannot be used because they are not stable and depolymerize to the monomer, S8. Inverse vulcanization reported recently uses vinylic monomers as crosslinkers to stabilize polymers made from elemental sulfur. Here we report that the catalyst sodium diethyldithiocarbamate trihydrate allows inverse vulcanization to be conducted at low temperatures (110 °C), even below the melting point of sulfur (120 °C). Lower reaction temperatures are beneficial for not only energy economy, but also in preventing dangerous auto-acceleration, hydrogen sulfide generation, and allowing low boiling point monomers to be used. Excess catalyst can be recovered from the polymers, and despite a crosslinked structure, the reversibility of the S-S bonds allows the polymers to be recycled.**

Introduction

Sulfur polymers have attracted attention in recent years, because of their potential to reduce reliance on ecologically damaging conventional synthetic polymers, and alleviating the “excess sulfur problem”.1–3 Synthetic polymers are widely used on a vast scale, however the majority of them are derived from petrochemicals, which are finite resources, contrary to green chemistry principles.4,5 Therefore, alternative materials made from industrial by-product or renewable biomass are sought. In order to decrease the emission of SO2 and prevent acid rain, sulfur is removed from petroleum and natural gas and eventually converted to elemental sulfur.1,2 Hence, elemental sulfur is incredibly cheap and readily available for use. It is reported that more than 70 million tonnes of elemental sulfur is produced annually, with much of it stockpiled at refining sites.2,3 Sulfur is used to prepare both commodity and specialty chemicals, such as sulfuric acid, fertilizers, and conventional vulcanization, but its supply significantly outweighs demand.2,3,6,7 Thus, sulfur polymers are one of the most promising candidates to consume redundant sulfur and to be an alternative to conventional synthetic polymers.

S8 polymerizes above 159 °C when sulfur radicals are generated from ring opening by homolytic cleavage and propagate to form linear polysulfide.6–9 However, the challenge accompanied with this reaction is that the polymeric sulfur generated is unstable and depolymerizes back to S8, by a back-biting mechanism, even at room temperature. Capping the sulfur radical ends by dienes, an inverse vulcanization process reported by Pyun, Char, and coworkers in 2013 is able to efficiently stabilize sulfur polymers against depolymerization.6,8,10 In this facile processing, high concentration sulfur diradicals were homopolymerised first, then the liner sulfuric chains were copolymerised with 1,3-diisopropenylbenzene (DIB), creating a highly branched thiopolymer. The novel polymeric material exhibited both outstanding optical and electrochemical properties. Inspired by this innovation, Charlker *et al.* synthesized new sulfur polymers by a renewable comonomer, limonene. Substitution by limonene as a comonomer could decrease the cost of processing and increase the experiment scales as limonene is a by-product in the citrus industry.7,11 Since then, various polyenes, such as divinylbenzene (DVB),12,13 dicyclopentadiene (DCPD),9 ethylene glycol dimethylacrylate (EGDMA),14–16 vegetable oil,17,18 myrcene,9 diallyl disulfide,19 perillyl alcohol,20 and ethylidene norbornene (ENB) were also studied to prepare low cost and sustainable sulfur polymers.15,21

Sulfur polymers have been studied for a variety of applications, for instance, LiS batteries,10,18,22 antimicrobial materials,23 controlled-release fertilisers,24 the stabilization of metal nanoparticles,25 oil–water separation,26 water purification,3,7–9 environmental remediation,7,15 and IR transparent lenses.12,27,28 For widespread practical applications to be realised, scaling the reaction up and simplifying the processing are two key challenges. Additionally, according to the principle of green chemistry, the design for reactions should consider energy efficiency and renewability as well. However, in the processing of inverse vulcanization, most reactions reported until now required reaction temperatures higher than 160 °C. Several different systems have been investigated to decrease the reaction temperatures. Dynamic Covalent Polymerizations were termed to prepare sulfur polymers at mild temperature, even as low as 60 °C, but required the synthesis of oligomers or prepolymers at higher temperatures first to generate activated sulfur radicals.29,30 Dynamic sulfur bonds were vital to this strategy, because of acting as an accelerator to reduce the reaction energy of the whole system. Thus, the disadvantage of complex operation cannot be overlooked. However, this modification made it possible to incorporate crosslinkers with lower boiling points into inverse vulcanization.29,30 Another main approach is applying catalyst in the system, a better way also aligned with green chemistry. But, to date, the temperature limitation was still fixed to 135 °C, a temperature required to melt sulfur then to generate sulfur radicals.15

Herein is reported a mild condition catalytic inverse vulcanization, in which the temperature is below 119 °C, at which sulfur remains in the solid state, to prepare stable sulfur polymers (figure 1). In this process any excess catalyst could be collected and recycled. It was supposed that the catalyst may lower the energy of reactions, likely acting as an initiator attacking and opening S8 at low temperature, allowing the activated sulfur chains to propagate in the whole system. Additionally, after leaching catalyst in the products, sulfur polymers could be remoulded into alternative shapes at 110 °C because of the S-S dynamic covalent bonds.

Experimental

Materials

Sulfur (S8, sublimed powder, reagent grade, ≥99.5%, Brenntag UK & Ireland. Purchased in 25 kg bags), ethylene glycol dimethylacrylate (EGDMA, 98%, Alfa Aesar), sodium diethyldithiocarbamate trihydrate (Alfa Aesar), 1, 3-diisopropenylbenzene (DIB, 97%, TCI), and methyl methacrylate (MMA, 99%, Sigma Aldrich) were commercially available and used as received.

Polymerisations

Reactants (5 g sulfur, 5 g crosslinker, and the associated amount of catalyst) were mixed in 40 mL volume glass vials by vortex, before being heated at the specified temperatures in aluminium blocks and stirred by magnetic stirrer bars for polymerisations. For DIB, heating in the aluminium block was required for a minimum of 12 hours in order to generate fully solid products, which were then further cured in an oven at 110 °C for 12 hours. For EGDMA, the reaction finished in 20 minutes to generate fully solid products, and further curing was conducted in the oven at 110 °C for 12 hours. For MMA, the reaction was conducted at 95 °C for more than 12 hours, and moved into an oven for further curing for 96 hours. Specific conditions and components for different samples are listed in table 1.

**Leaching and remolding**

Sulfur polymer SDIBC10T110 was ground into fine powder and washed by water. Supernatant was evaporated after

Table 1. Samples trialed with different components and under different conditions.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Sample name\* | Crosslinker /% | NaDTC /% | Temperature/°C | Reacting time and curing time |
| SEGDMAC1T100 | EGDMA 50% | 1 | 100 | 20 min; overnight (>12 hours) |
| SEGDMAC1T110 | EGDMA 50% | 1 | 110 | 10 min; overnight (>12 hours) |
| SDIB30C1T110 | DIB 30% | 1 | 110 | Incomplete reaction of sulfur |
| SDIBC1T110 | DIB 50% | 1 | 110 | >12 hours, <24 hours; overnight (>12 hours) |
| SDIBC5T110 | DIB 50% | 5 | 110 | >12 hours, <24 hours; overnight (>12 hours) |
| SDIBC10T110 | DIB 50% | 10 | 110 | 12 hours; overnight (>12 hours) |
| SDIBC0T180 | DIB 50% | 0 | 180 | 10min; no curing |
| SMMAC10T95 | MMA 50% | 10 | 95 | >12 hours, <24 hours; 96 hours (curing temperature raised from 95 °C to 110 °C gradually) |
| SEGDMAC0T110 | EGDMA 50% | 0 | 110 | No reaction |
| SDIBC0T110 | DIB 50% | 0 | 110 | >40 hours; overnight (>12 hours) |
| SMMAC0T95 | MMA 50% | 0 | 110 | No reaction |

\*Naming system: sulfur polymers are referred to as S–Crosslinker-P-C-n-T-n, where P is the percentage of crosslinkers used in the experiments, if the ratio of sulfur to crosslinker is 1:1, P will be omitted, C-n refers to weight percentage of catalyst, and T-n shows the temperature reactions were conducted.

centrifugation to recrystallize the catalyst. Residual solid powder was dried and transferred into a silicone mold and reheated at 110 °C in the oven for 48 hours to remold.

Results and discussion

Sulfur polymers Sodium diethyldithiocarbamate trihydrate (NaDTC) has been used as a rubber accelerator in industry,31 and this inspired us to apply this chemical into inverse vulcanisations. However, for some reactions, it reacted too quickly and generated inhomogeneous products, or even resulted in auto-acceleration from the Trommsdorff-Norrish effect at the standard heating temperature (higher than 135 °C) of inverse vulcanizations.15 Therefore, this phenomenon encouraged us to trial this chemical to initiate and accelerate inverse vulcanization at low temperature. Moreover, was noticed that the organic ligand of NaDTC seemed to benefit the miscibility of the system compared with inorganic catalysts, such as Na2S. Conventionally, inverse vulcanization has been performed at a temperature higher than 135 °C to induce cleavage of sulfur rings and generate disulfur radicals. But in the reaction at lower temperature, sulfur rings were possibly opened heterogeneously by nucleophilic activation.29 Considering that sulfur is solid at below 120 °C, the reaction is conducted in two phases, thus the ratio of sulfur to crosslinkers is important as too much sulfur (such as Sample SDIB30C1T110, see Table 1 footnote for naming system) decreases mobility of the system, resulting in inhomogeneous products, as shown figure S1, in ESI). Sulfur polymers were prepared as stable solids at low temperature with different colours as shown in figure 1 (b). The difference in colour appears to depend on the degree of reaction and the length of sulfur chain, as the more catalyst applied the darker product is.

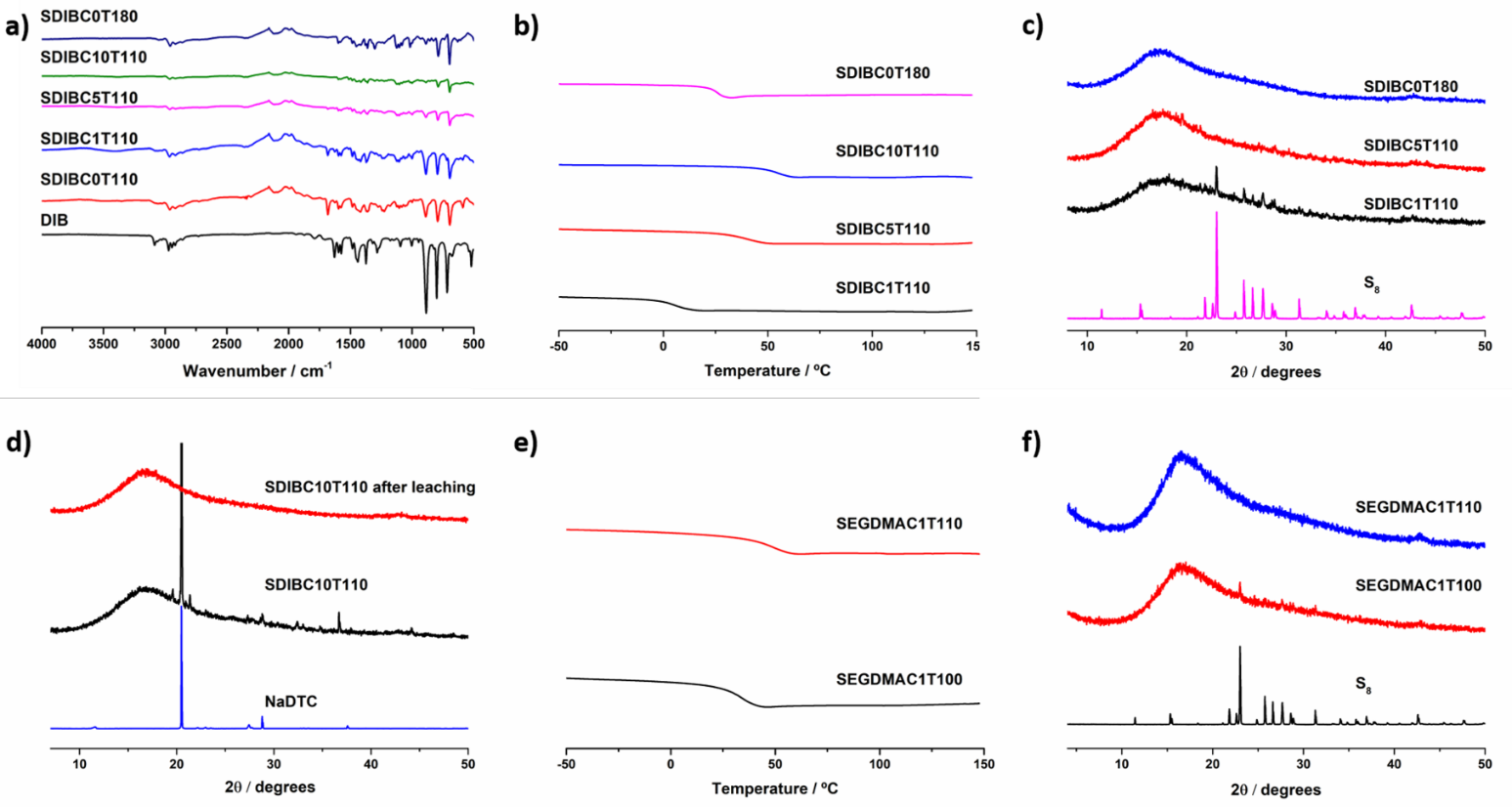


Figure 2. (a) FT-IR spectroscopy of sulfur polymers with different amount catalyst. (b) Offset DSC traces for different percentage NaDTC of poly(S-DIB). (c) Offset PXRD patterns for different percentage NaDTC of poly(S-DIB). (d) Offset PXRD patterns for SDIBC10T110 and corresponding residual solid after leaching, and NaDTC. (e) Offset DSC traces for different temperatures of poly(S-EGDMA) with NaDTC. (f) Offset PXRD patterns for poly(S-EGDMA) synthesized at different temperatures with NaDTC.

Poly(S-DIB)

The reactions (e.g. SDIBC0T110) without catalyst at low temperature were conducted as control experiments. Surprisingly, it was found that even with no catalyst DIB could react with solid sulfur but prohibitively slowly. From the 1H NMR (figure S2, ESI) performed at 18 hours, there were some new peaks appearing between 3.0 and 4.0, indicating the generation of S-C bonds. This is the first time inverse vulcanization has been observed below the sulfur melting temperature (figure S3, ESI). However, because it took more than 40 hours for the reaction to reach completion without catalyst, this would be problematic for practical use. The reactions of sulfur and DIB with catalyst are initially heterogeneous. After 2 hours, all visible solid sulfur was either dissolved or reacted with no more solid remaining (figure S4, ESI), but the reaction still remained heterogeneous in that two distinct liquid layers could be seen. Around 7 hours, the degree of reaction determined by NMR was similar to that of SDIBC0T110 at 18 hours (figure S2, ESI). We also compared the 1H NMR of SDIBC10T110 assumed same time with SDIBC0T110, indicating that the reaction with NaDTC is much more complete at same temperature (figure S2, ESI). Sulfur polymersmade at low temperature were from light yellow to dark brown, changing with the amount of catalyst. These colours are similar in appearance to these of conventionally produced sulfur polymers. Increased catalyst content in the reaction is likely to lead to increased C=C double bond reaction, and shorter S-S chains between crosslinkers. The ATR-FTIR patterns, as shown in figure 2a and S7, of Poly(S-DIB) further confirmed this assumption. As the amount of catalyst is increased, reductions of signals were shown at 3080, 3041, and 1640 cm-1, corresponding to the stretching and symmetric stretching vibrations of C=C-H and stretching vibration of C=C respectively. Moreover, the clear decrease of signals at 887 cm-1, of the CH2 out-of-plane deformation, verified more C=C double bounds are consumed in the reaction with increased catalyst content. According to the result of elemental analysis, the actual sulfur content of SDIBC1T110 was found to be higher than that calculated in theory, probably because of the evaporation of monomers during the reaction processing (as shown in Table S1, ESI). From the DSC traces, as shown in figure 2 (b) and figure S6, ESI, *T*g increased with the amount of catalyst. In comparison with the thiopolymer produced from S and DIB without catalyst (but at the higher temperature of 180 °C), sulfur polymers generated from the reaction with 1% catalyst had lower *T*g, however the products of both reactions with 5% and 10% catalyst had higher *T*g. There is no sulfur melting peak observed from all sulfur polymers. Powder X-ray diffraction (PXRD) was also used to detect if residual sulfur crystals are present in the amorphous copolymers. Interestingly, from powder X-ray diffraction patterns of all poly(S-DIB), as shown in figure 2 (c) and (d), different sharp peaks could be observed, some of which do not match the pattern of any sulfur polymorph. After further study, the patterns observed in SDIBC5T110 and SDIBC10T110 were identified as that of NaDTC, indicating the presence of residual catalyst in the polymers. Additionally, to test the degree of the reaction and the stability of product, any amorphous sulfur imbedded in the polymers synthesized after 3 months was detected by ﻿thin layer chromatography (TLC). The result (figure S7, ESI) shown no sulfur could be detected from SDIBC10T110, suggesting the totally consumption of elemental sulfur and the stability of S-S bonds. The reaction was increased from 10 g to 100 g to demonstrate the potential for scaling up (figure S8, ESI), benefiting industrial processing.

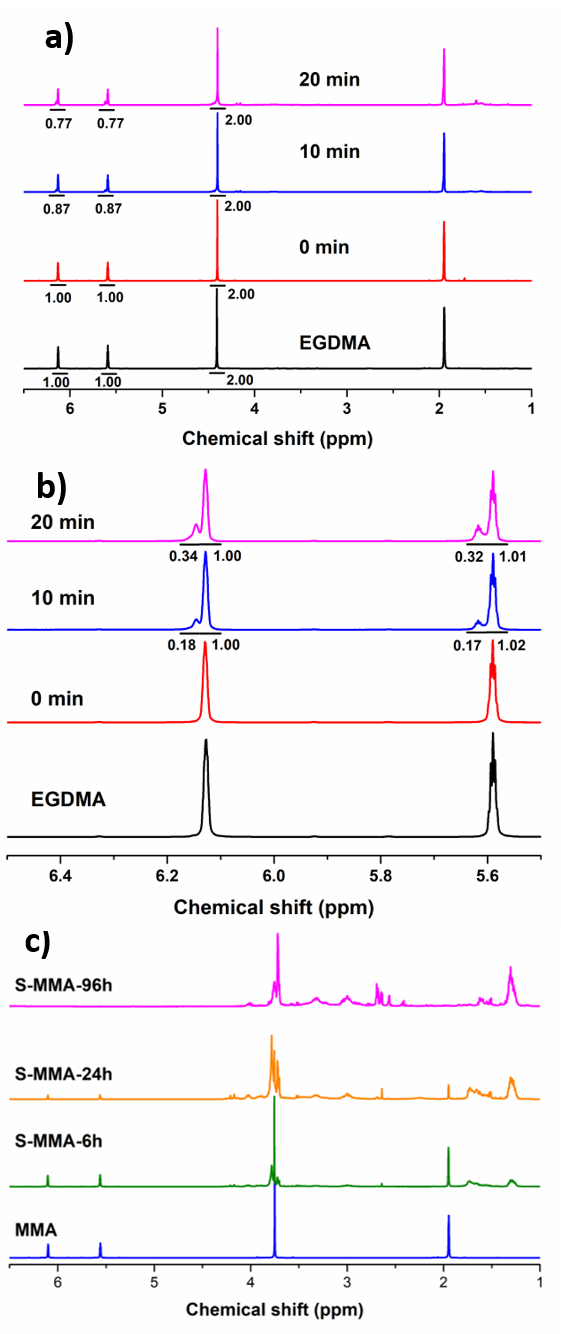


Figure 3. (a) 1H NMR spectra for the reaction of sulfur-EGDMA from 0 min to 20 min, and the integral of vinyl protons reduced. (b) Peaks of vinyl protons shifted to downfield. (c) 1H NMR spectra for the reaction of sulfur and MMA at different time. Apparently, after further curing, vinyl groups were totally reacted.

Poly(S-EGDMA) AND Poly(S-MMA)

Similar to the control experiments of sulfur and DIB, SEGDMAC0T110 and SMMAC0T95 were performed, as shown in figure S9, ESI. However, unlike SDIBC0T110, sulfur did not react with either EGDMA or MMA at low temperature for more than 18 hours, which were confirmed by 1H NMR (Fig S10 and figure S11, ESI). Invloved NaDTC, EGDMA reacted heterogeneous with sulfur initially at mild temperatureand became homogeneous at last (figure S12, ESI). From the DSC traces (see figure 2 (e) and figure S13, ESI), sulfur polymers prepared from EGDMA at different temperature (100 or 110 °C) have clear glass transition temperatures, indicating the generation of homogenous copolymers. There is no significant difference the *T*g, suggesting that the reacting temperature did not affect reaction processing very much. In both situations, no S8 crystals were detected. A higher ratio of catalyst added to the reaction of sulfur and EGDMA further increased the rate, but also trigged auto-acceleration, introducing heterogeneity (figure S14, ESI). From the diffraction patterns of poly(S-EGDMA) (figure 2 (f)), a small signal of crystalline elemental sulfur could be detected from the sample made at 100 °C, but there was no sharp peak observed from the sample made at 110 °C. With the same amount of catalyst, the reaction time of S and EGDMA was much shorter than that of S and DIB, giving an opportunity to screen the reaction through 1H NMR in the early stage of polymerisation. As the reaction proceeds (figure 3(a)), the integral ratio of the peaks at 5.6 and 6.1 to the peak at 4.4 reduced, indicating the decreasing of C=C double bonds. Interestingly, new peaks appeared next to both peaks assigned as C=C bond protons, and also the ratio of the new shifted peaks to the original peaks increased, as shown in figure 3(b). We speculate that new peaks are shifted from the original positions because of polymerization of sulfur onto the double bond at the other end of the molecule. However, we have to point out that hydrogen substitution is also a possibility. The product prepared from S and MMA is more like oligomer or low molecular weight branched polysulfide than a thiopolymer, and unlike poly(S-DIB) and poly(S-EGDMA), all products of S-MMA could be dissolved in deuterated chloroform. Gel permeation chromatography (GPC) was used to test the molecular weight of S-MMM, showing results of *M*w= 740 g mol-1 and *M*w/*M*n = 1.22 (figure S15, ESI). After curing and removing from the oven, the product was a homogeneous wax-like material, however, cooling to room temperature, 30 min later, phase separation could be observed, and sulfur crystals were precipitated. This was probably because with only one C=C bond in MMA, it was difficult to stabilize too much sulfur. The reaction was followed by 1H NMR as well, as shown in figure 3(c). Two peaks indicating alkenyl hydrogens reduced and finally disappeared after long term curing. However, it is hard to say there is no homopolymerisation by MMA, but, from the peaks around 3, the reaction between sulfur and MMA could be confirmed. However, from the comparison between 1H NMR spectra for S-MMA-96h and PMMA, it could be concluded that copolymerization of sulfur is dominant reaction instead of homopolymerization of MMA (figure S16, ESI).

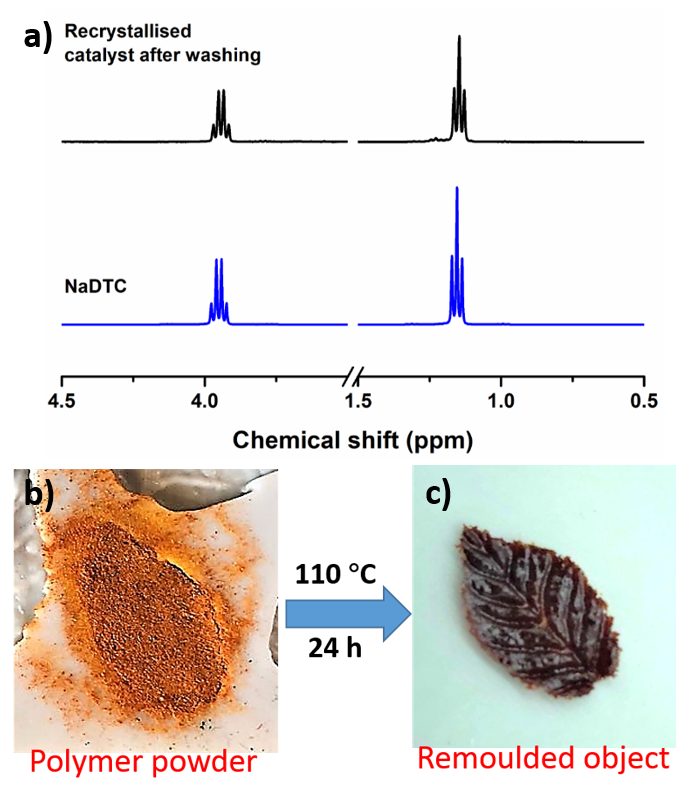


Figure 4. (a) 1H NMR spectra for residual solid crystallised after leaching and standard NaDTC. (b) Washed powder was transferred in silicone mould. (c) Remoulded sample from reprocessing in the oven at 110 °C.

In order to further prove the catalyst could be used in inverse vulcanization at mild temperature, benefiting crosslinkers with low boiling point, ﻿1,4-cyclohexanedimethanol divinyl ether (CDE) was induced to react with elemental sulfur directly. CDE was previously used as a crosslinker in mild temperature reported by Jenkins *et al*.30 However, in their report they found that CDE could not be reacted directly with sulfur below its boiling point, rather a prepolymer made by reacting sulfur with another crosslinker at high temperature was needed to generate dynamic sulfur bonds which then activate the low temperature reaction of the mixed crosslinker system. For the direct sulfur-CDE system, catalyzed by NaDTC, several characterizations confirmed that CDE reacted with S8 completely at 110 °C in only one step (figure S17, ESI).

Leaching and remolding

As residual catalyst was detected by PXRD, the sulfur polymers was ground into fine powder and washed with water, attempting to separate the polymer and catalyst. After washing and centrifugation, the supernatant was evaporated to crystalize residual catalyst. The yield of recrystallisation was only 7.9%, mainly because some catalyst is likely still trapped in the sulfur polymers. From NMR results, as shown in figure 4(a), the crystalized products have the same pattern as pure NaDTC along with other impurity peaks. This indicates there is the potential for recycling of any excess catalyst used. In the rubber industry, the term catalyst is often used for additives included to increase the rate of vulcanization, largely because it is not possible to separate them back out of the material and reuse them. As such, the term catalyst may not be technically appropriate. In this report, NaDTC has been termed as a catalyst instead of accelerator because it is a more broadly recognized term. After drying, the washed polymers were retested by PXRD. The pattern showed no crystallinity remained. After reheating in the oven, the fine powder could be remolded into different shapes (figure 4(b) and (c)). In the reforming processing, with residual catalyst trapped in the sulfur polymers, the S-S bonds were activated as dynamic covalent bonds, even at the low temperature of 110 °C.

Conclusions

Different sulfur polymers were successfully synthesized by inverse vulcanization below the sulfur melting temperature, with NaDTC as a catalyst. Chemically stable and shape-persistent high-sulfur-content copolymers could be generated. Through this method, no solvents or pre-reacted species were required, and residual catalyst could also be recovered, aligned with the principles of green chemistry. It should be considered that the time taken for the reaction will also contribute to the energy costs, as well as the temperature itself. That noted, this catalytic route allows lower temperatures to be used, or shorter reaction times for a given temperature. Lower temperatures allow lower boiling crosslinkers to be more easily incorporated, and may be required if sulfur polymers are to be combined with other temperature sensitive materials. Additionally, after washing, the sulfur polymers could be reprocessed at mild temperature, allowing recycling. Thus, a new route to inverse vulcanize at low temperature is provided.

Acknowledgements

We thank L. Qie for useful discussion on NMR. T.H.thanks the Royal Society for a Research Fellowship.

Conflicts of interest

There are no conflicts to declare.

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